

X. *On the Laws of Connexion between the Conditions of a Chemical Change and its Amount.* By A. VERNON HARCOURT, M.A., Student of Christ Church, and Demonstrator of Chemistry in the University of Oxford; and WILLIAM ESSON, M.A., Fellow of Merton College, Oxford\*. Communicated by Sir B. C. BRODIE, Bart., F.R.S., Professor of Chemistry in the University of Oxford.

Received September 5,—Read November 16, 1865.

### I. *On the Reaction of Permanganic and Oxalic Acids.*

WHEN any substances are brought together under circumstances under which they act chemically one upon another, a change takes place which consists in the disappearance of a part of the original substances and the appearance of an equal weight of other substances in their place. This change continues, if the circumstances remain the same, until the whole of one of the substances taking part in it has disappeared. Its total amount is therefore ultimately determined by the amount of that substance which was originally present in the smallest proportional quantity. The attainment of this limit, as will be shown, requires theoretically an infinite time, but the velocity of chemical change is so great that the practical limit of an inappreciable residue is in most cases speedily reached. Owing perhaps to this fact, chemists have been led to bestow their chief attention upon the result, and not upon the course of these changes. Occupied in investigating the relation between the reagents and the ultimate products of a reaction, and studying the chemical and physical properties of the thousand different substances thus produced, they are accustomed to regard the various conditions under which every chemical change takes place, and by which its amount is determined, chiefly as means to an end, as points to be attended to in a receipt for preparing one substance from another.

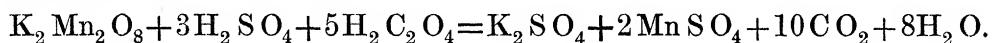
The object of the investigation which the authors have the honour of laying before the Royal Society in the following pages, has been to estimate quantitatively the relation of chemical change to some of these conditions. With this view they have selected for examination cases in which the change appeared to be of a simple character, and the conditions affecting it few in number, and capable of being defined.

Although unquestionably every chemical reaction is governed by certain general laws relating to the quantity of the substances partaking in it, their temperature and physical state, and the time during which they are in contact, yet the number of cases in which the investigation of these is practicable is extremely limited. In the first place, it must

\* The experimental inquiries recorded in this paper were chiefly Mr. HARCOURT's, the mathematical discussion is Mr. ESSON's.

be possible both to start and terminate the reaction abruptly at a given moment. In the next, either some product or some residue of the action must be a substance for whose estimation exact and ready methods are known, that so the amount of change may be quantitatively determined. Lastly, all the conditions of the reaction must be measurable, or at least definable, and some of them susceptible of modification at will, that thus the influence of each may be examined.

The first reaction chosen by us for investigation was that of permanganic acid upon oxalic acid. It is well known that when a solution of potassic permanganate is added to a solution containing oxalic acid and sulphuric acid, its red colour gradually disappears, owing to the reduction of the permanganic acid. The final result of the change is thus represented :



This reaction occurs at a temperature which is easily kept constant and can be exactly measured. It occupies, under duly arranged conditions, a convenient interval of time. The reagents and the products of the reaction are all soluble, and thus the system can quickly be made and will remain homogeneous. The reagents are readily obtained in a state of purity, and divided and measured as liquids. The reaction can be stopped abruptly, and the residual permanganic acid estimated, by adding to the solution potassic iodide and determining volumetrically the amount of iodine liberated. Lastly, no variation of light, such as occurred in the course of experimenting\*, or of atmospheric pressure, or of any other condition besides those that have been named, affects the result. But the action is not chemically simple. The various complications which it exhibits will be discussed as they are revealed by successive experiments. One of these occasions the well-known change of colour from red to brown, which the liquid undergoes as the action proceeds. The manganous sulphate which is formed by the reduction of the higher oxide reacts upon the remaining permanganic acid, producing one or more intermediate oxides which combine with oxalic acid. And since the formation and reaction of manganous sulphate could not be avoided, it became necessary to include this salt among the reagents, the effect of whose variation was to be determined.

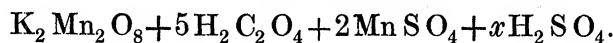
#### A. Variation of Sulphuric Acid.

The following experiments were made in order to discover the variation in the amount of chemical change due to a variation in the amount of sulphuric acid, the other conditions of the reaction being kept constant. In every experiment the solution contained  $\text{K}_2\text{Mn}_2\text{O}_8$ , *i. e.*, 316·2 parts of permanganate of potassium,  $5\text{H}_2\text{C}_2\text{O}_4$ , and  $2\text{MnSO}_4$ . The absolute weight of potassic permanganate used in each experiment was ·014 gramme, the volume of the solution was 330 cub. centims., its temperature  $16^\circ\text{C}$ ., and the time allowed to elapse between the mixture of the ingredients and the termination of the action was four minutes. The action was terminated by the sudden addition of an excess

\* Direct sunlight produces a great acceleration.

of potassic iodide, by which the remaining permanganate is instantaneously reduced. The amount of iodine set free, which had previously been proved to furnish an exact measure of the permanganate, was finally determined by means of a standard solution of sodie hyposulphite.

TABLE I.



Volume of solution 330 cub. centims. Temperature 16° C. Time 4 mins.

1. Molecules of sulphuric acid. <i>x.</i>	2. Cub. centims. of hyposulphite used.	3. Percentage of oxidizing residue. <i>y.</i>	4. Percentage of chemical change. $100 - y.$
2	(1) 28·4	(2) 28·4	78·2
4	23·45	23·05	64·0
6	17·9	17·55	48·9
8	13	13·5	36·5
10	10·3	.....	28·4
12	8·25	8·2	22·6
14	6·4	6·4	17·6
16	5·25	5·1	14·3
22	2·8	.....	7·7
			92·3

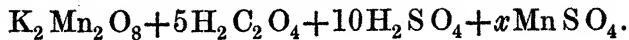
When no oxalic acid was taken and the whole amount of permanganate was represented by its equivalent of iodine, there were used to decolorize the solution 36·3 cub. centims. of hyposulphite.

The numbers in column 3 are obtained by making this number 100, and reducing the mean of those in column 2 to the same scale. It will be seen that the amount of chemical change occurring within the allotted time increases continually with the quantity of sulphuric acid in the solution, the effect, however, of successive increments being less and less. This relation is exhibited by the annexed curve (Plate XVII. fig. 1). In spite of the apparent simplicity of the conditions of these experiments and of the progressive variation introduced, no simple relation could be discovered between the two series of numbers. It will be shown subsequently, by the light of later experiments, that the relation between them is of a very complex character. Two molecules of manganous sulphate were added to the mixture, that the rate might not be disturbed by its gradual formation. The part played by this salt appearing particularly worthy of investigation, was made the subject of the next series of experiments.

### B. Variation of Sulphate of Manganese.

All the conditions adopted in the first series were repeated in this, with the exception that ten molecules of sulphuric acid were used in each experiment, and the amount of manganous sulphate was varied.

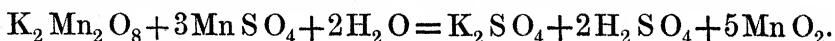
TABLE II.



Volume of solution 330 cub. centims. Temperature 16° C. Time 4 mins.

1. Molecules of sulphate of manganese. <i>x.</i>	2. Cub. centims. of hyposulphite used.	3. Percentage of oxidizing residue. <i>y.</i>	4. Percentage of chemical change. $100 - y.$
0·0	36·0 (1) ..... (2)	99·2	0·8
0·25	35·25	97·2	2·8
0·5	34·5	95·3	4·7
0·75	34·25	93·9	6·1
1·0	32·7	90·3	9·7
1·25	31·35	86·4	13·6
1·5	28·45	78·4	21·6
1·75	18·5	52·3	47·7
2·0	10·8	29·9	70·1
2·25	7·45	20·6	79·4
2·5	6·0	17·1	82·9
2·75	5·85	16·0	84·0
3·0	5·6	15·4	84·6
4·0	5·4	14·9	85·1
5·0	5·35	14·7	85·3
10·0	5·15	14·2	85·8

It appears from these experiments, the results of which are depicted (Plate XVII. fig. 2), that the effect of increasing the amount of manganous sulphate in the solution is to accelerate the action to a small extent only when the quantity added is small, but rapidly when it exceeds one molecule, until at the point where three molecules are taken, a rate is attained which is hardly increased by any further addition. This maximum rate is first reached with that quantity of manganous sulphate which is capable of reacting with the potassic permanganate to form binoxide of manganese,



In the succeeding experiments at least three molecules of manganous sulphate were always introduced into the solution, that the gradual formation of this salt as the reduction of the permanganate proceeds might not complicate the result. As to the manner in which manganous sulphate acts, the gradual changes which took place in the appearance of the fluid bore conclusive testimony. Though the final result, whenever not less than three molecules of this salt were present, was nearly the same, the liquid passed from a pink to a brown colour more rapidly as the quantity was increased, and with the largest proportion it became first turbid, and then comparatively clear again, before the four minutes had elapsed.

### C. Variation of Oxalic Acid.

Two series of experiments were made in order to determine the effect of varying the proportion of oxalic acid which takes part in the reaction. In one of these only potassic permanganate, manganous sulphate, and oxalic acid were employed; in the

other there was added also a constant quantity of sulphuric acid. To prevent the action being inconveniently slow, the volume of the solution was reduced to 100 cubic centimetres. The numerical results are contained in the following Tables, and are expressed by the curves in Plate XVII. figs. 3 & 4.

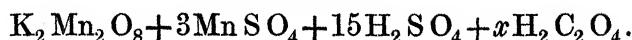
TABLE III.



Volume of solution 100 cub. centims. Temp. 16° C. Time 3 mins.

1. Molecules of oxalic acid. <i>x.</i>	2. Cub. centims. of hyposulphite.	3. Percentage of oxidizing residue. <i>y.</i>	4. Percentage of chemical change. $100-y$ .
0	36.3	100.0	0.0
1	29.85	82.2	17.8
2	25.95	71.5	28.5
3	23.5	64.7	35.3
4	21.85	60.2	39.8
5	20.5	56.5	43.5
6	21.0	57.9	42.1
7	23.35	64.3	35.7
8	31.85	87.8	12.2
9	33.4	92.0	8.0
10	33.55	92.4	7.6
11	33.8	93.1	6.9
15	33.85	93.3	6.7
20	33.6	92.6	7.4
30	33.5	92.3	7.7
50	31.95	88.0	12.0
100	29.45	81.8	18.2

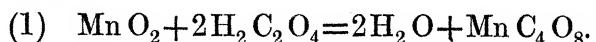
TABLE IV.



Volume of solution 100 cub. centims. Temperature 16° C. Time 3 mins.

1. Molecules of oxalic acid. <i>x.</i>	2. Cub. centims. of hyposulphite.	3. Percentage of residue. <i>y.</i>	4. Percentage of chemical change. $100-y$ .
0	36.1	100.0	0.0
1	28.7	79.5	20.5
2	20.85	57.7	42.3
3	13.4	37.1	62.9
4	8.0	22.2	77.8
5	4.55	12.6	87.4
6	3.0	8.3	91.7
7	5.5	15.2	84.8
8	13.85	38.4	61.6
9	26.55	73.6	26.4
10	29.95	83.0	17.0
11	31.25	86.6	13.4
12	31.85	88.2	11.8
15	32.6	90.3	9.7
20	32.95	91.3	8.7
30	32.85	91.0	9.0

It will be seen that in both cases the quantity of permanganate reduced in three minutes increases with the proportion of oxalic acid up to a certain point; it then diminishes again until another point is reached; after which further additions of oxalic acid produce once more a very gradual acceleration. The first part of this result is readily intelligible. The rate at which the reduction proceeds is greater with a larger amount of the reducing agent. But why does a still larger amount produce an opposite effect? The explanation is to be found no doubt in another circumstance by which this reaction is complicated. When solutions of manganous sulphate and potassic permanganate are mixed, a precipitate of hydrated manganic binoxide is produced, which soon separates from the liquid, leaving it colourless if the manganous salt were in excess\*. The presence of a sufficient quantity of oxalic acid prevents this precipitation; a clear brown liquid is formed whose colour very slowly fades, the reduction in a cold and dilute solution occupying many hours. This solution, like that of cupric oxide in potash containing a reducing substance, depends no doubt upon a chemical combination which precedes the mutual action of oxidation and reduction. Probably the brown liquid contains oxalate of manganic binoxide. In the experiments with oxalic acid only, the maximum action in three minutes occurs very near that point at which the amount of oxalic acid present is five molecules, or the quantity which the measure of permanganic acid can oxidize. If, as the experiments with manganous sulphate appear to prove, the first stage of the reaction consists in the formation of manganic binoxide, this maximum action occurs with one molecule of binoxide and one of oxalic acid. The subsequent minimum again nearly coincides with that point at which ten molecules of oxalic acid have been added for one of permanganate, or two for one of binoxide. It was also observed that whenever a less amount than this was taken, the liquid became turbid, but with this or any larger amount it remained clear. According to analogy, oxalate of manganic binoxide should have the formula  $MnO_2 \cdot 2C_2O_3$ , or  $MnC_4O_8$ . For its formation two molecules of oxalic acid are required. The final action, when not less than two molecules of oxalic acid have been taken, may therefore be thus represented:

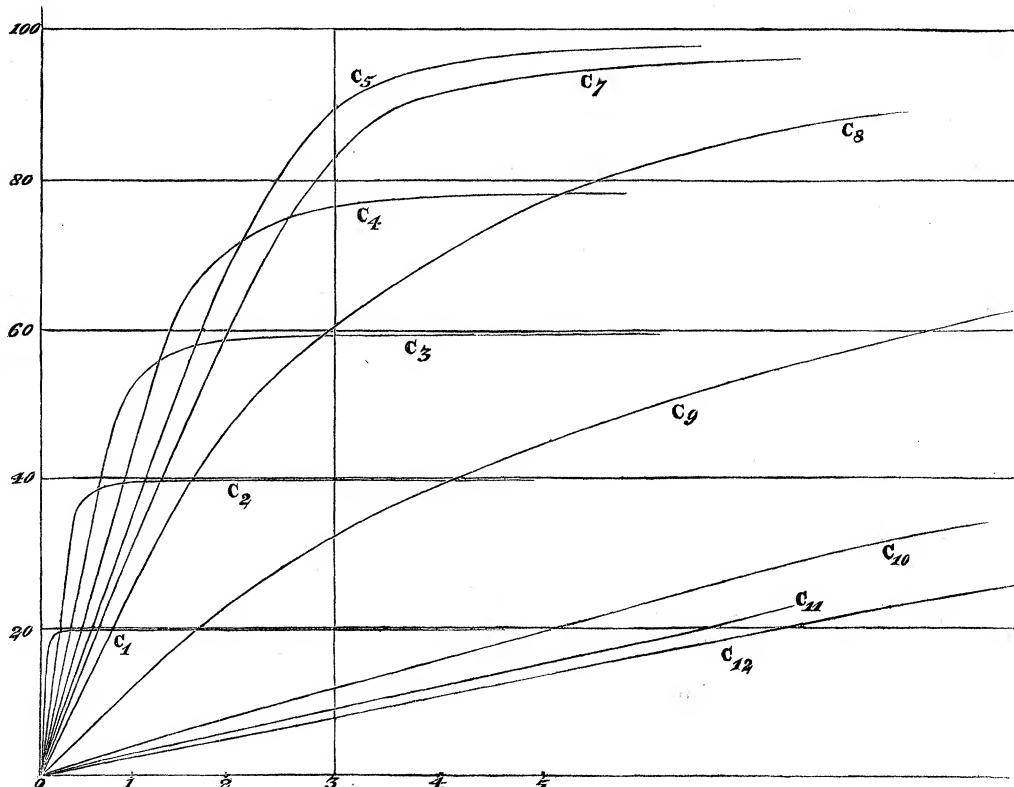


The decomposition of this salt takes place more slowly than does the oxidation of oxalic acid by free binoxide of manganese; it is accelerated by the presence of sulphuric acid, or of a great excess of oxalic acid.

In the second series of experiments, in which sulphuric acid was introduced, the amount of action is at first proportional to the amount of oxalic acid taken, for within the allotted three minutes the whole is oxidized. Afterwards the total reduction effected within this time is still increased by the addition of a fourth and fifth and

\* In this case the precipitate consists of  $5MnO_2$ ,  $MnO$ .—GORGEU, 'Ann. de Chim. et de Phys.' 3rd series, vol. lxvi. p. 153.

even of a sixth molecule; but the increase is no longer in direct proportion, but in a less ratio. The explanation already suggested appears to be in accordance with all the phenomena both of this and of the first series. The rate at which a given amount of oxalic acid is oxidized diminishes as the total amount present increases up to that point at which enough has been added to convert the potassic permanganate and manganous sulphate into oxalate of manganic binoxide and a potassium salt. With one molecule the rate at which its oxidation proceeds is very great, but when it is complete, the percentage of chemical change cannot exceed twenty. Accordingly it attains this limit in the second series, and nearly approaches it in the first. With two molecules the rate is less, and still less with three, but the proportion oxidized in any time is a less proportion of a larger quantity. When five molecules have been added, the total amount of chemical change possible cannot be increased, since this quantity is sufficient to reduce the whole of the permanganate. Consequently the amount oxidized in any time is thenceforward a less proportion of the same quantity. The annexed diagram, in which the course of each experiment is represented by a separate curve having for its asymptote a line parallel to the axis of  $x$  at a distance representing the total amount of chemical change possible after the lapse of any length of time, may serve for illustration.



$x$  = time;  $y$  = percentage of chemical change; C<sub>1</sub>, C<sub>2</sub>, ... C<sub>12</sub> curves representing the action with 1, 2, ... 12 molecules of oxalic acid.

The experimental numbers in the two Tables are to be regarded as a series of measurements of the distance of a point on each curve from the axis of  $x$ , along an ordinate whose distance from the axis of  $y$  represents an interval of three minutes.

Sulphuric acid appears to accelerate the reaction in two ways. First, it promotes the action of manganic binoxide on oxalic acid; and secondly, it retards the formation of the comparatively stable compound, which in its absence is at once produced on mixing the three other ingredients. This is shown by the persistency of the red colour of permanganic acid in a mixture containing a large proportion of sulphuric acid. To the former cause principally must be attributed the greater rate of change throughout the second series, and to the latter the circumstance that in this case the maximum action occurs with rather more than five molecules, and the subsequent minimum with more than ten. It seems probable that with a large excess of sulphuric acid the rate at which the reduction proceeds would be found to vary directly with the quantity of oxalic acid, according to the law which appears to exist in other similar cases.

#### D. Variation of Time.

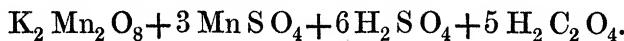
One of the conditions which has been kept constant hitherto, is the time during which the reaction has been allowed to proceed. But in order to discover the exact effect of each chemical or physical variation, it is necessary to be acquainted with the whole course of the reaction, and not merely with the amount of change accomplished under each set of circumstances during one interval of time. Now, by performing a number of experiments only differing one from another in the period which is allowed to elapse between starting and stopping the reaction, we may trace its course with any required degree of minuteness. And if we can discover the relation of the series of numbers representing the duration of the several experiments to those representing the corresponding amounts of chemical change, an expression may be thence deduced for the rate at which the reaction is proceeding at a given time, or with a given quantity of substance, and a comparison made between the rates derived from different series of experiments.

If it were possible for all the conditions of a chemical change to remain constant, if, for example, the substances reacting could be added in proportion as they disappeared, and those formed either were without influence or could be removed, the effect of a variation of time might be confidently predicted. In such a case the total amount of chemical change would be directly proportional to the duration of the action. But where one or more of the substances diminishes in quantity as the change proceeds, the relation is no longer of this simple character.

The following series of experiments, in which only the duration of the reaction was varied, had for its object the discovery of this relation. The various substances were employed in the proportions in which they react with one another, except the sulphuric acid, of which a double portion was taken. After the other solutions had been mixed and brought to the right volume and temperature, the measure of potassic perman-

ganate, 0·014 grm. in 10 cub. centims. of water, was added and rapidly mixed with the rest. The moment of its addition was noted, and when the proper interval had elapsed an excess of potassic iodide was thrown in. The amount of iodine liberated was then determined.

TABLE V.

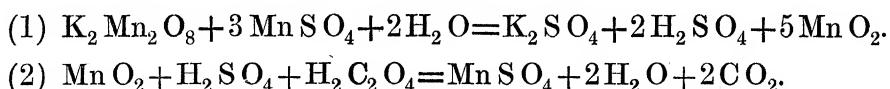


Volume of solution 330 cub. centims. Temp. 16° C. Time  $x$  mins.

1. Duration of experiment, in minutes. $x$ .	2. Percentage of oxidizing residue. $y$ .	3. Percentage of chemical change. $100 - y$ .
1	95·6	4·4
2	83·2	16·8
3	66·8	33·2
4	55·2	44·8
5	44·5	55·5
6	36·3	63·7
7	31·6	68·4
8	27·2	72·8
9	25·0	75·0
10	22·5	77·5
15	13·5	86·5
17	11·8	88·2

This series of determinations may be regarded as exhibiting the course of a single experiment in which the reaction is allowed to proceed during seventeen minutes. Of a hundred parts of the oxidizing and reducing substances (or transferable oxygen, or chemical energy) originally present, there remain after one minute 95·6 parts, after two minutes 83·2 parts, and so on. Throughout the middle part of the course of this experiment, from the end of the fourth to the end at any rate of the tenth minute of its progress, a relation exists between the corresponding numbers in the first and second columns which strikes the eye at once. Their product is a constant quantity. The divergence of the results for the fifteenth and seventeenth minutes is probably due to an experimental error, committed either in determining the rather small amount of residue, or in the measurement of the proportional quantities of the two principal reagents; such an error would affect chiefly the later stages of the experiment, the ratio of the two substances which should be constant changing slowly at first and afterwards more rapidly. But the divergence of the result in the earlier part of the experiment is much more considerable, and shows unmistakeably that, until the reaction has advanced a certain distance, it does not follow the hyperbola which correctly represents the remainder of its course. The same fact, it will be seen, reappears in every similar series of experiments. Its cause was for a long time obscure, and the authors were driven to discard this relation, which appeared only to hold good for part of their results, and to be inconsistent with others of equal authority. Later experiments, however, have established the reality of this relation, and led to the discovery of the cause of divergence.

The reaction under consideration has already been shown to occur in two stages, in the first of which manganic binoxide is produced by the reaction of permanganic acid on manganous sulphate, and in the second of which it is reduced by oxalic acid, after previous combination, when that acid is present in excess.



Unfortunately both these reactions belong to the class, comparatively rare in inorganic chemistry, of slow actions. If either of them occurred very rapidly as compared with the other, the curve representing the reaction of proportional quantities would doubtless be a hyperbola from its starting-point. As it is, the first action takes place more rapidly than the second, their relative rates varying, however, according to the conditions of each experiment. In the present case the first action has nearly attained its limit at the end of four minutes, and thenceforward the only change taking place is that which the second equation expresses. After this time the simple law already enunciated holds good, and the residues become inversely proportional to the duration of the action. In this case the actual moment of starting the experiment happens, through the complication of the double action, to be the true epoch from which to reckon its duration. But in other cases it is not so: the zero of the series of numbers representing the time should correspond to an infinite amount of the active substances, and not to 100 parts. The full discussion of the significance of this relation, and of the course of the reaction when the two changes are occurring simultaneously, is reserved until the entire series of experiments has been brought forward; but it may be shown that the inverse proportionality of the residue to the time depends upon a law the generality of which we hope hereafter to establish, namely, that the total amount of chemical change varies directly with that of each of the substances partaking in it.

Let  $x$  = the duration of the action dated from a point such that when  $x=0$ ,  $y=\infty$ ; and let  $y$  = the number of molecules of the oxidizing and reducing substances present in the solution at the time  $x$ . Then  $\frac{dy}{dx}$  is the amount of change in a unit of time, and this is proportional to  $y^2$ , since both substances are changing, and the amount of change varies directly with the quantity of each of them. Hence we have the equation

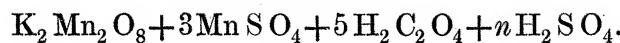
$$\frac{dy}{dx} \propto -y^2 = -\frac{1}{k} \cdot y^2,$$

which gives

$$xy=k, \text{ or } y \propto \frac{1}{x}.$$

The following Table contains the results of three similar series of experiments, differing from the last and from one another only in respect of the quantity of sulphuric acid used in each.

TABLE VI.

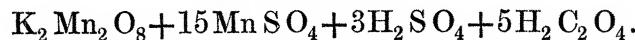
Volume of solution 330 cub. centims. Temperature 16° C. Time  $x$  mins.

Duration of experiment, in minutes. $x.$	Percentage of oxidizing residue.		
	$n=12.$ $y.$	$n=18.$ $y.$	$n=24.$ $y.$
1	94.5	93.3	
2	76.2	73.2	
3	52.0	39.6	30.8
4	37.8	24.3	17.9
5	28.5	18.6	13.1
6	23.3	14.5	10.4
7	19.7	12.0	7.6
8	16.7	9.6	
9	14.5	7.6	

These numbers present a less obvious relation than those of the first series, but it may be observed in all, after the fourth minute, that if the numbers representing the time, minus about one minute, be multiplied into the corresponding amounts of residue, the product is approximately a constant quantity,  $(x-x_0)y=k$ . But in fact each successive series is less and less conformable to this relation. Probably the increase in the amount of sulphuric acid produces this effect by diminishing the disproportion between the two rates before mentioned, for its action is to retard the formation of manganic binoxide, and to hasten its reduction by oxalic acid.

With a smaller quantity of sulphuric acid and a larger quantity of manganous sulphate more satisfactory results were obtained, but it was not found possible, when only a proportional quantity of oxalic acid was employed, to hinder the solution from becoming turbid through separation of manganic binoxide. The use of a large volume of water prevents the occurrence of this turbidity, but impairs too far the accuracy of the subsequent determinations. The series of experiments recorded in the following Table traces the course of the reaction with an excess of manganous sulphate, and proportional quantities of each of the other substances, through its entire length.

TABLE VII.

Volume of solution 100 cub. centims. Temperature 16° C. Time  $x$  mins.

1. Duration of exper- iment, in minutes. $x.$	2. Percentage of oxidizing residue. $y.$	3. Values of $y$ , calculated from $(x+1)y=157.$	4. Percentage of chemical change. $100-y.$
0.25	91.0	.....	9.0
0.5	81.0	.....	19.0
1	65.8	.....	34.2
2	51.9	.....	48.1
3	42.4	.....	57.6
4	35.4	.....	64.6
5	29.8	.....	70.2
6	25.7	25.7	74.3
7	22.2	22.1	77.8
8	19.4	19.4	80.6
9	17.3	17.3	82.7
10	15.5	15.5	84.5
15	10.4	10.4	89.6
20	7.8	7.8	92.2
30	5.5	5.2	94.5
40	4.4	3.9	95.6

It will be seen that after six minutes the residues still un-reduced are inversely proportional to the time during which the action has continued. In the earlier stages of the reaction its rate follows a less simple law, probably for the reason already stated—the gradual though relatively rapid action of permanganic acid on the excess of manganous salt. The actual modification thus introduced will be considered subsequently, and it will be shown that, from an equation in which account is taken of this action, the earlier numbers may be calculated as well as the later. A curve representing this series will be found in Plate XVII. fig. 6. The duration of the reaction is measured along the axis of  $x$ , and the remaining chemical energy along the axis of  $y$ . The former is an asymptote of the curve: the absolute disappearance of the oxidizing and reducing substances requires theoretically an infinite time. The other asymptote falls just beyond the axis of  $y$ : no amount of binoxide can be taken so great, as that with it this reaction should proceed for six minutes and six seconds, and still leave a residue of 25.7 parts. The best equation for the lower part of this curve is  $(x+0.1)y=157$ .

In the foregoing series of experiments the principal reagents have been employed in the proportions in which they act one upon another, that so their ratio might remain constant throughout. The same result may be approximately attained by taking very large quantities of all the reagents except one, or at least such quantities that the alteration which they undergo in the course of the experiment can produce no appreciable effect upon the rate at which the chemical change is proceeding. It is most convenient to select the substance of which the residue can be determined as that of which a relatively small quantity is to be employed. The conditions of the reaction under these circumstances are indeed simpler than in the former case; for then each of the substances acting on one another is diminished, and thus two or more variations are made simultaneously, while in this case a single substance gradually disappears, all around it remaining unchanged.

Accordingly solutions were prepared of the different reagents, of such a strength as that one measure of each should contain a large excess, as compared with the amount contained in one measure of the standard solution of potassic permanganate.

The actual quantities used in each experiment were the following:—

	Potassic permanganate.	Manganous sulphate.	Oxalic acid.	Sulphuric acid (one unit).	Water.
Weight in grammes ...	0.015	0.1	0.648	0.352	
Molecules .....	1.0	13.9	108.4	75.8	
Proportional parts .....	1.0	4.6	21.7	25.3	

By proportional parts are meant those quantities which react according to the equations before written.

The method of performing these experiments underwent various modifications during

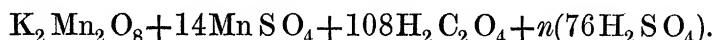
their course. That which was finally adopted for this and the concluding set may be here briefly described. Different series of experiments differed from one another only in the proportion of sulphuric acid employed, and the several experiments of the same series differed only in the time during which the reaction was allowed to proceed. One description therefore will serve for all; and to render this description more precise, let it refer particularly to the eighth series of the present set. In the first place, a mixture was made to serve for all the experiments of the series by bringing together in a large flask 200 cub. centims. of the standard solutions of oxalic acid and manganous sulphate, each of these solutions containing in 10 cub. centims. the amount required for one experiment, 400 cub. centims. of standard sulphuric acid containing in 10 cub. centims. four units, and 3000 cub. centims. of water. This mixture was exactly divided by means of a narrow-necked flask marked to hold 190 cub. centims., among twenty flasks each of about 300 cub. centims. capacity. One of these was taken and its contents brought to a temperature of 16° C. It was then placed in an arrangement for keeping the temperature constant, consisting of an inner and outer casing, supported over a lamp, the interval between which was filled with water at a temperature of 16°. The interior of the inner casing was lined with cotton-wool, and it was provided with a lid similarly lined, which could be slipt over the neck of the flask. A delicate thermometer passed into the fluid through a disk of cardboard, by which the flask's mouth was closed. The standard solution of potassic permanganate was contained in a bottle encased in the same manner, and was maintained at the same temperature. A clock beating seconds served to measure the duration of the experiments. When the thermometer stood constantly at 16°, a 10 cub. centims. pipette was charged with the permanganate solution, the flask was removed for a moment from its receptacle, and the liquid in the pipette allowed to run into it, starting by beat of the clock at the beginning of a minute. By shaking round the flask as the liquid entered, the whole was perfectly mixed at the end of about ten seconds. If the temperature had suffered any disturbance, it was raised or lowered by the application of the hand or of a damp cloth. The flask was then replaced, and required but little attention until the time for stopping the reaction approached.

For determining the residue, we have made use of a standard solution of sodic hyposulphite. This reagent, according to our experience, is liable to a gradual alteration by which its reducing power is slightly diminished, a few particles of sulphur being at the same time separated from it. The addition of a minute quantity of caustic soda prevents the occurrence of this change, and renders the value of the solution absolutely constant. Just before the allotted time had elapsed a measure of potassic iodide solution, containing rather more than enough to reduce the permanganate originally taken, was poured into a test-tube; the flask was then removed from its casing, and at the proper moment the contents of the test-tube were discharged into it. By a single rapid shake the iodide is diffused through the liquid, and all the molecules of peroxide which have

escaped the slow action of oxalic acid are instantaneously reduced, leaving in their stead so many molecules of iodine, which are without action on any ingredient of the solution and can therefore be estimated at leisure. By using a very dilute solution of hyposulphite, and a freshly prepared and filtered solution of starch, the subsequent determination may be performed with a high degree of accuracy. Some of the measured quantities of the mixed solution were always reserved for a repetition of previous experiments; in several instances the whole series was performed twice. In these latter sets the readings of the burette, after two similar experiments, seldom differed by more than 0·15 cub. centim. From time to time the value of the measure of permanganate was taken in terms of the solution of hyposulphite, and the numbers given in the Tables as the percentage of residue are obtained by multiplying the actual readings on the burette by 100, and dividing by this number.

The following Table contains the results of fifteen series of experiments thus conducted. Their object was twofold, to establish by a sufficient induction the true course of the reaction, and to discover by a comparison of the different series the relation between the rate of change and the quantity of sulphuric acid employed. The curves representing this series of experiments will be found on Plate XVIII. fig. 1.

TABLE VIII.



Volume of solution 200 cub. centims. Temperature 16° C. Time  $x$  mins.

Duration of experiment, in minutes. $x.$	Percentage of oxidizing residue.						
	$n=1.$ $y.$	$n=2.$ $y.$	$n=3.$ $y.$	$n=4.$ $y.$	$n=5.$ $y.$	$n=6.$ $y.$	$n=7.$ $y.$
$\frac{1}{2}$	.....	.....	.....	92·9	91·4	.....	88·7
1	94·4	91·9	89·2	86·8	83·1	81·2	79·1
$1\frac{1}{2}$	.....	.....	.....	81·6	76·9	73·4	69·6
2	90·4	86·3	81·1	76·8	70·6	66·4	61·6
$2\frac{1}{2}$	.....	.....	.....	.....	.....	.....	54·9
3	86·7	80·0	73·5	67·2	59·8	54·7	49·0
$3\frac{1}{2}$	.....	.....	.....	.....	.....	.....	43·9
4	82·3	74·6	66·7	59·1	51·5	45·3	39·5
5	78·8	.....	60·9	52·6	44·4	37·9	32·4
6	75·5	65·2	55·3	47·0	38·5	31·9	26·9
7	71·8	.....	50·6	41·8	33·4	27·7	22·2
8	68·4	58·1	46·3	37·3	29·7	23·3	
9	.....	.....	42·5	.....	26·4	19·8	
10	62·1						

TABLE VIII. (continued).

Duration of experiment, in minutes. <i>x.</i>	Percentage of oxidizing residue.						
	<i>n</i> =8. <i>y.</i>	<i>n</i> =9. <i>y.</i>	<i>n</i> =10. <i>y.</i>	<i>n</i> =11. <i>y.</i>	<i>n</i> =12. <i>y.</i>	<i>n</i> =13. <i>y.</i>	<i>n</i> =16. <i>y.</i>
$\frac{1}{2}$	.....	.....	84·5				
1	74·5	73·3	70·4	67·4	64·1	61·6	57·2
$1\frac{1}{2}$	64·5	.....	58·5	54·8	51·4	47·3	41·4
2	56·3	53·0	48·7	44·9	40·8	37·3	30·7
$2\frac{1}{2}$	49·2	43·7	41·0	36·9	32·5	29·2	23·1
3	43·2	38·8	34·2	30·5	26·8	23·3	17·5
$3\frac{1}{2}$	38·1	33·8	29·2	25·4	21·6	18·7	13·9
4	33·6	29·3	25·2	21·6	17·8	15·5	11·2
$4\frac{1}{2}$	.....	.....	21·7	18·1	15·1	12·9	9·2
5	27·2	22·6	18·6	15·5	13·0	.....	7·5
6	21·6	.....	14·5	.....	9·7	8·0	5·5
8	.....	.....	.....	.....	.....	4·4	
9	12·3	.....	.....	.....	5·9		

It will be seen that by varying the quantity of sulphuric acid from 25 to 400 proportional parts, the reaction is caused to take place with very different velocities. Under the conditions of the last set of experiments more work is done in one minute than is done in ten minutes under the conditions of the first set. In how orderly a manner the amount of residue diminishes as the reaction proceeds, and the rate of change increases with the proportion of sulphuric acid, is shown by the series of curves on Plate XVIII. fig. 1, corresponding to this Table. Guided by the empirical relation which we had observed in the case of the reaction of proportional quantities, we endeavoured to apply the hyperbola to these curves also. It soon became evident, especially from those experiments in which the reaction proceeded rapidly and was traced through a greater length, that the rectangular hyperbola was not applicable. A hyperbola with an oblique asymptote corresponded much more nearly to our experimental lines, and a number of equations of the form  $y^2 + axy - by = c$  were obtained, which gave values of *y* nearly agreeing with those which had been found. But after calculating the constants of this equation for each series of experiments, we observed, 1st, that the earlier and later numbers never agreed quite so well as the rest, the disagreement with the best possible equation at the two extremes generally rather exceeding the probable error of experiment; 2ndly, that when a curve was produced upwards, as could be done by repeating the series with a larger quantity of permanganate, the divergence became much greater; and 3rdly, that instead of the actual numbers falling in an irregular manner above and below those calculated from the equations,—as was to be expected if experimental error alone were the cause of difference,—a regular rise and fall was perceptible, the calculated numbers being in every case lower than the first observation or two, then higher than the two or three following, then lower again for four or five consecutively, and finally rising once more above them. Consequently these equations could not be accepted as expressing truly the course of the reaction, and it was therefore vain to

inquire how their constants were related to the number of units of sulphuric acid employed. Some other expression for the course of the reaction had to be sought, and a consideration of the circumstances under which the reaction now takes place furnished the needful clue.

If any quantity of a substance be placed under conditions under which it gradually undergoes a change, and if both the conditions and the quantity of the substance be by a due system of compensation kept constant, the rate of change will be uniform; that is to say, the amount of substance which disappears in a unit of time will be always the same. This amount therefore, for any particular unit of time, is a certain fixed proportion of the total quantity undergoing change. If, now, the system of compensation be so far disturbed as that while other conditions remain the same the quantity of substance be allowed to diminish, it seems probable that the total amount of change occurring at any moment will be proportional to the quantity of substance then remaining.

Adopting this hypothesis, the law of connexion between the quantity of substance remaining at any time, and the time during which the change has proceeded, may be found in the following way:—

Let  $y$  represent the amount of substance remaining after the change has proceeded for a time  $x$ , and let  $dy$  be the diminution of the substance during an infinitesimal time  $dx$ , then  $\frac{dy}{dx}$  represents the amount of substance which disappears in a unit of time; and this amount is by the hypothesis proportional to the quantity of substance remaining; so that we have the equation

$$\frac{dy}{dx} = -\alpha y,$$

which gives

$$y = ae^{-\alpha x},$$

where  $\alpha$  is the quantity of substance at the commencement of the change.

This equation expresses the fact that the quantities of substance remaining after a series of intervals of time increasing in arithmetical progression, form a series in geometrical progression. After the intervals 0, 1, 2, 3, ... minutes, the quantities of substance remaining are

$$a, \quad ae^{-\alpha}, \quad ae^{-2\alpha}, \quad ae^{-3\alpha}, \quad \dots,$$

a geometric series of which the ratio is  $e^{-\alpha}$ . The curve which expresses this relation between  $x$  and  $y$  is a logarithmic curve.

As the actual determinations of the oxidizing residue had been made at equal intervals of time, it was an easy matter to test the applicability of this hypothesis. It appeared that although these numbers were in most cases nearly in geometrical progression through a considerable range, they were not so throughout, and the values of  $y$  calculated on this hypothesis differed more from the experimental values than those before obtained from the equation of an oblique hyperbola. A single experiment, however, made at the close of this series, in which no sulphuric acid was taken, showed

that the relation indicated by theory did, under some circumstances, actually hold good. The numerical results of this experiment are compared below with the values of  $y$  calculated from the equation  $y=94\cdot8(0\cdot974)^x$ , and are represented by a curve on Plate XVII. fig. 5.

TABLE IX.



Volume of solution 200 cub. centims. Temperature 16° C. Time  $x$  mins.

Duration of experiment, in minutes. $x.$	Oxidizing residue.		Duration of experiment, in minutes. $x.$	Oxidizing residue.	
	Found. $y.$	Calculated. $y.$		Found. $y.$	Calculated. $y.$
2	94·8	94·8	31	44·0	44·0
5	87·9	87·6	35	39·1	39·6
8	81·3	80·9	44	31·6	31·2
11	74·9	74·7	47	28·3	28·8
14	68·7	69·0	53	24·2	24·6
17	64·0	63·7	61	20·2	19·9
27	49·3	48·9	68	17·0	16·5

Generally the reaction appeared to proceed more slowly in its later as compared with its earlier stages than on this hypothesis it ought. It seemed possible that this might arise from the excess of the various reagents employed not having been sufficient to prevent the action producing a sensible alteration in the nature of the solution, and thus affecting the rate; for unless the amount of each of the other substances be so great as compared with that whose rate of diminution is measured that the quantity subtracted from or added to them is relatively insignificant, the simplicity of the case under examination is no longer ensured. Accordingly a second set of experiments was made, in which, the amount of permanganate employed being the same, a still larger proportion was used of the other reagents; and by making two preliminary series of experiments, in one of which the same quantity was taken at the beginning of the reaction as had been present in the other at the end, namely, 99 proportional parts of sulphuric acid and oxalic acid, instead of 100 of each, and 11 parts of manganous sulphate, instead of 10, it was proved absolutely that these changes did not affect the rate, for the numbers of the two series were nearly identical.

The numerical results of this set are contained in the following Table, and are expressed by the curves (Plate XVIII. fig. 2).

TABLE X.



Volume of solution 200 cub. centims. Temp. 17° C. Time  $x$  mins.

Duration of experiment, in minutes. $x$ .	Percentage of oxidizing residue.					
	$n=1.$ $y.$	$n=3.$ $y.$	$n=4.$ $y.$	$n=5.$ $y.$	$n=8.$ $y.$	$n=10.$ $y.$
1	.....	87.9	82.8	77.4	60.0	48.2
1½	.....	.....	.....	.....	45.9	
2	92.9	77.3	.....	59.7	35.9	23.9
2½	.....	.....	.....	.....	28.0	
3	.....	67.7	56.2	45.7	22.6	13.5
3½	.....	.....	.....	.....	18.3	
4	84.5	58.5	.....	36.0	15.4	8.3
4½	.....	.....	.....	.....	12.7	
5	.....	51.4	38.6	.....	10.5	5.1
5½	.....	.....	.....	.....	9.1	
6	76.5	.....	.....	22.7		
7	.....	39.4	26.8	17.9		
8	68.9	.....	.....	14.7		
9	.....	30.1	18.7			
10	61.9	.....	.....	9.2		
11	.....	22.8	13.1			
12	54.9	.....	.....	5.5		
13	.....	17.2	9.2			
14	48.9	.....	.....	4.4		
15	.....	13.4	6.7			
17	.....	10.3	4.1			
18	37.8					
19	.....	7.7				
22	30.0					
23	.....	4.3				
26	24.4					
30	17.8					
34	14.0					
40	10.4					
46	6.8					

Of these experiments three series, those with 300, 400, and 500 proportional parts of sulphuric acid, give numbers which conform approximately to the relation  $y = ae^{-\alpha x}$ , but the more rapid action which occurs with 800 and with 1000 parts of acid cannot be expressed by an equation of this form. The excess of the other reagents over that which suffers reduction is as great, and that of the sulphuric acid greater, in these than in the first experiments. Some other cause than a change in the medium in which the gradual action takes place must therefore produce this departure from the theoretical result. Comparing the former set of determinations with these, it appears also that the divergence in both is of the same kind, and therefore presumably due to the same cause. In both the ratio of the descending series gradually diminishes. The true reason is probably to be found in the fact that more than one gradual change takes place under the circumstances of our experiments, and that we have only been able to measure the total result. Our attempts to separate these actions and investigate them singly have

been unsuccessful, and we have been compelled in consequence to leave the examination of this reaction, and seek for a simpler case of chemical change. We may, however, in concluding this part of our work, show, first, from independent experiments, that we have probably been dealing with more than one reaction; and secondly, that numbers agreeing with those of all the experimental series may be calculated from equations expressing the hypothesis that three simultaneous changes take place.

In determining the amount of free iodine at the end of each experiment, some difficulty was experienced from the rapid return of the blue colour after its removal by the last drop of hyposulphite, and it was found necessary to allow as short a time as possible to elapse between the addition of potassic iodide and the determination. The conditions of this gradual oxidation of hydriodic acid were afterwards examined, and it was found that the action was due neither to the oxalic acid nor the manganous sulphate, nor any other of the reagents employed, but occurred only in the fluid in which the gradual oxidation of oxalic acid had taken place, and that moreover the rate of its occurrence depended upon the quantity of oxalic acid thus oxidized. Some experiments were made in which this secondary oxidation was allowed to reach its limit. The action of the air, which in presence of manganous salt, when the solution is let stand for many hours, is apt to be considerable, was rendered as small as possible by boiling out the water used and keeping the liquid under carbonic acid; a correction for it was also obtained from a comparative experiment. It appeared that the secondary oxidation did not exceed one-sixth of the primary, and bore to it often a still smaller proportion, while at the same time its amount was always sufficient to leave no doubt as to the reality of the phenomenon. The available oxygen of the permanganate is thus finally distributed in two ways, part of it remaining in a form in which it acts gradually on hydriodic acid, and another larger part having no such action. What oxidizing substance the colourless solution still contains, whether a less reducible salt of manganese, or some compound produced, as is most likely, by the gradual oxidation of oxalic acid, we do not know; but the fact that some substance is formed besides a manganous salt, carbonic acid, and water, is certain. If, however, two products, or any number of different products, are formed by the action, according to different equations, of one oxidizing substance—binoxide of manganese, for example,—the quantities of this substance remaining after equal intervals of time should still be in geometric progression; for the amounts of each of the products which is formed at any given time is proportional to the whole amount of binoxide present in solution at that time, and in consequence the amount of binoxide which disappears owing to the formation of each of the products is also proportional to the whole amount of binoxide present.

Let  $d_1y$ ,  $d_2y$ , ...  $d_ny$  be the amounts of binoxide which disappear during an infinitesimal time  $dx$ , owing to the formation of  $n$  different products, then  $\frac{d_1y}{dx}$ ,  $\frac{d_2y}{dx}$ , ...  $\frac{d_ny}{dx}$  are the amounts of binoxide which disappear in a unit of time owing to their formation, and each of these is proportional to the whole amount  $y$  of binoxide present at a time  $x$ ;

hence

$$\frac{dy}{dx} = -\alpha_1 y, \quad \frac{d_2y}{dx} = -\alpha_2 y, \dots \quad \frac{d_ny}{dx} = -\alpha_n y;$$

but if  $dy$  is the whole amount of binoxide which disappears in the time  $dx$ , we have

$$dy = d_1y + d_2y + \dots + d_ny,$$

and therefore

$$\frac{dy}{dx} = -(\alpha_1 + \alpha_2 + \dots + \alpha_n)y,$$

or

$$y = ae^{-(\alpha_1 + \alpha_2 + \dots + \alpha_n)x},$$

a logarithmic curve of the same type as that obtained in the case in which only one product is formed.

But since the proportions of the reagents and all other conditions of the reaction have been kept rigorously constant, we may presume that between any two reagents only one reaction occurs. If, therefore, oxalic acid yields both the normal products of its oxidation, carbonic acid and water, and also the substance, whatever it may be, which acts slowly on hydriodic acid, it is probable that it is oxidized by more than one reagent. The following experiments supply some further evidence that oxalic acid may hold dissolved two distinct manganic oxides, and be attacked by them at different rates; or—if, as we have supposed, solution here is due to combination—that two manganic oxalates may be formed whose rates of decomposition are different.

A solution was prepared of manganous-manganic sulphate by dissolving a quantity of manganous sulphate in dilute sulphuric acid, and saturating the liquid with hydrated manganic binoxide. The brown precipitate dissolves slowly and sparingly, forming a deep-red solution, which is completely decomposed by the addition of a sufficient quantity of water. A second solution was made of potassic permanganate of equal oxidizing power when measured by hydriodic acid. The rate at which each was reduced by oxalic acid in presence of equal quantities of manganous sulphate and sulphuric acid was determined, and the two rates found to be very nearly the same. A third series of determinations was made under the same conditions, excepting that no manganous sulphate was taken, with hydrated binoxide of manganese suspended in so much water as made a measure of it equivalent to a measure of the former solutions. For half a minute, until the binoxide was dissolved, the action took place rapidly; but when the liquid became clear, it proceeded more slowly for an equal amount of oxidizing residue than in the other solutions. This solution, therefore, differs from the former, which so far resemble one another, both in appearance and in rate of decomposition, as to render it likely that the chief agent is in both cases the same.

The direct action of permanganic acid on oxalic acid at a temperature of 16° or 17° is very gradual; perhaps if every trace of lower oxides of manganese and of other reducing agents than oxalic acid could be excluded, no action whatever would take place. But whether this be so or not, it may certainly be disregarded in comparison with the almost

instantaneous reaction between permanganic acid and manganous salt; for when the two solutions are mixed, the deep-red colour of the former is at once destroyed and the liquid becomes dark brown. The action of these two substances under constant conditions takes place presumably according to but one equation, and gives rise to but one oxidized product. From the results of our experiments on the "Variation of Manganous Sulphate," p. 195, and the reaction of the two substances when oxalic acid is not present, this product appears to be manganic binoxide. But in the experiment just related with the three equivalent solutions, the liquid produced by acting on permanganate with a great excess of manganous sulphate nearly identified itself by its rate of decomposition with that containing the salt of the proto-sesquioxide, while it differed in this respect from that into which binoxide had been introduced.

The account of the changes occurring under the circumstances of the two sets of experiments, Tables IX. and X., to which these observations appear to lead, is the following.

By the reaction of permanganic acid on a great excess of manganous sulphate there is formed at once manganic binoxide; we may therefore consider this oxide to be contained in the liquid at the moment of starting the reaction. It finds itself in presence of two substances, both of which act gradually upon it, oxalic acid and manganous sulphate, the latter producing an intermediate oxide, probably the proto-sesquioxide, which is also reducible by oxalic acid. It is possible that other oxides besides these may be formed, but it is almost certain from our experimental results that the action is not more simple than this. At the end of each experiment both these oxides are alike instantaneously reduced by hydriodic acid, and thus measured conjointly.

A mathematical discussion of various theoretical points that have been raised in the course of our experiments is appended to this account of them. It is there shown that the equation embodying the above hypothesis is

$$y = \frac{\alpha}{\alpha + \beta - \gamma} \{ \beta e^{-\gamma x} + (\alpha - \gamma) e^{-(\alpha + \beta)x} \},$$

where  $\alpha$  is the amount of binoxide present in the solution at the commencement of the action,  $\alpha$  the fraction of it which disappears in a unit of time by the action of the oxalic acid,  $\beta$  the fraction of it converted into the other oxide, and  $\gamma$  the fraction of this lower oxide which disappears in a unit of time.

In the following Tables some of the numbers obtained in the preceding experiments (pp. 206 & 210) are compared with those calculated from equations of this form. It will be seen that in general the three fractions upon which the whole rate of action depends increase as the sulphuric acid is increased, and that  $\alpha$  increases more rapidly than  $\gamma$ ;  $\alpha$  being first less than  $\gamma$ , then equal to it, and finally greater.

The number and exactness of our experimental results are not, however, sufficient to make the calculation of the three constants in these equations more than approximate, and thus no such comparison can be made of the rates of change with different amounts of sulphuric acid as might serve to reveal how these quantities are related. In the first of the following Tables the residues of the two oxidizing substances at the time of each

determination are given separately for two series; in the second Table several other series are compared with numbers similarly calculated according to the equations written over them.

TABLE XI.

Residues of oxidizing substance calculated from the equations

$$u = ae^{-(\alpha+\beta)x}, \quad v = \frac{a\beta}{\alpha+\beta-\gamma} \{e^{-\gamma x} - e^{-(\alpha+\beta)x}\}, \quad y = u+v,$$

where  $u$  and  $v$  are the residues of the primary and secondary oxide, and  $y$  is the total residue.

1. Case $\gamma > \alpha$ (Second set (p. 215) $n=1$ ).				2. Case $\alpha > \gamma$ (Second set (p. 215) $n=8$ ).			
$x.$	$u.$	$v.$	$y.$	$x.$	$u.$	$v.$	$y.$
0	37.4	0	37.4	1	11.6	11.0	22.6
2	21.0	13.8	34.8	1½	5.8	11.2	17.0
4	11.8	19.9	31.7	2	2.9	10.4	13.3
6	6.7	22.0	28.7	2½	1.5	9.0	10.5
8	3.7	22.0	25.7	3	0.7	7.8	8.5
10	2.1	20.8	22.9	3½	0.4	6.5	6.9
12	1.2	19.1	20.3	4	0.2	5.6	5.8
14	0.7	17.4	18.1	4½	0.1	4.6	4.7
18	0.4	13.8	14.2	5	0.0	3.9	3.9
22	0.2	11.0	11.2	5½	0.0	3.3	3.3
26	0.1	8.7	8.8				
30	0.1	6.7	6.8				
34	0.0	5.4	5.4				
40	0.0	3.7	3.7				
46	0.0	2.6	2.6				

TABLE XII.—Comparison of found and calculated results.

(The calculated numbers are derived from equations of the form  $y = a_1 e^{-\alpha_1 x} + a_2 e^{-\alpha_2 x}$ ).

## 1. First set.

$n=10.$ $y = 28.5(82)^x + 2.7(98)^x.$			$n=11.$ $y = 29(785)^x + 3.1(97)^x.$			$n=12.$ $y = 29.4(76)^x + 3.5(96)^x.$		
$x.$	$y.$		$x.$	$y.$		$x.$	$y.$	
	Found.	Calculated.		Found.	Calculated.		Found.	Calculated.
½	25.85	25.9	1	20.8	20.8	1	20.0	20.1
1	21.55	21.4	1½	16.9	16.9	1½	16.05	15.9
1½	17.9	17.8	2	13.85	13.8	2	12.75	12.6
2	14.9	14.9	2½	11.4	11.3	2½	10.15	10.2
2½	12.55	12.5	3	9.4	9.4	3	8.35	8.3
3	10.45	10.4	3½	7.85	7.8	3½	6.75	6.8
3½	8.95	9.0	4	6.65	6.7	4	5.55	5.6
4	7.7	7.8	4½	5.6	5.6	4½	4.7	4.7
4½	6.65	6.6	5	4.7	4.8	5	4.05	4.1
5	5.7	5.8				5½	3.5	3.5
6	4.45	4.5				6	3.0	3.0
						9	1.85	1.9

TABLE XII. (continued).

## 2. Second set.

$n=1.$ $y=42\cdot7(94)^x - 5\cdot3(75)^x.$			$n=3.$ $y=37\cdot9(873)^x.$			$n=4.$ $y=32\cdot6(842)^x + 5\cdot3(676)^x.$		
$x.$	$y.$		$x.$	$y.$		$x.$	$y.$	
	Found.	Calculated.		Found.	Calculated.		Found.	Calculated.
2	34.75	34.8	1	32.9	33.1	1	31.0	31.0
4	31.75	31.7	2	28.95	28.9	3	21.05	21.0
6	28.6	28.7	3	25.4	25.2	5	14.45	14.4
8	25.75	25.7	4	21.9	22.0	7	10.05	10.0
10	23.1	22.9	5	19.3	19.2	9	7.0	7.1
12	20.55	20.3	7	14.85	14.7	11	4.9	5.0
14	18.3	18.1	9	11.35	11.2	13	3.45	3.4
18	14.15	14.2	11	8.55	8.6	15	2.5	2.4
22	11.2	11.2	13	6.45	6.6	17	1.55	1.7
26	8.95	8.8	15	5.0	4.9			
30	6.7	6.8	17	3.85	3.8			
34	5.25	5.4	19	2.9	2.9			
40	3.9	3.7	23	1.6	1.7			
46	2.55	2.6						
$n=5.$ $y=33\cdot7(794)^x + 4\cdot2(501)^x.$			$n=8.$ $y=25\cdot2(689)^x + 20\cdot8(251)^x.$			$n=10.$ $y=31\cdot4(417)^x + 6\cdot4(75)^x.$		
$x.$	$y.$		$x.$	$y.$		$x.$	$y.$	
	Found.	Calculated.		Found.	Calculated.		Found.	Calculated.
1	29.05	28.9	1	22.5	22.6	1	18.05	17.9
2	22.4	22.3	1 $\frac{1}{2}$	17.1	17.0	2	8.95	9.0
3	17.1	17.4	2	13.4	13.3	3	5.1	5.0
4	13.5	13.6	2 $\frac{1}{2}$	10.5	10.5	4	3.1	3.0
6	8.5	8.6	3	8.5	8.5	5	1.9	1.9
7	6.7	6.7	3 $\frac{1}{2}$	6.9	6.9			
8	5.5	5.3	4	5.8	5.8			
10	3.4	3.4	4 $\frac{1}{2}$	4.8	4.7			
12	2.1	2.1	5	3.9	3.9			
14	1.6	1.3	5 $\frac{1}{2}$	3.4	3.3			

The actual readings of the burette are given above instead of the amounts per cent., in order to show more clearly what is the practical limit of error in this mode of experimenting. The earlier series of numbers in the first set (Table VIII.) are omitted, because they are not sufficiently prolonged to be characteristic. Of the second set that corresponding to three proportions of sulphuric acid is perfectly geometric, while those on either side of it, corresponding respectively to one and to four proportions of acid, are not. It will be shown that this curious circumstance depends upon the existence of a particular relation between two of the three rates.

The foregoing experiments prove that the reaction here examined is of a complex character, and thus unsuited to the purpose with which we entered upon this investigation. The law that the amount of chemical change in a unit of time is proportional to that of each of the substances reacting, rather serves to explain these results than is

established by them. Its truth, however, appears to be demonstrated in another and simpler case of chemical change which we have since examined, and therefore it may now be fairly applied to the elucidation of results which when first obtained were uninterpretable.

On this simpler case—the reaction occurring between hydriodic acid and peroxide of hydrogen—we have made numerous series of experiments, varying in succession each condition of the reaction. The results of this investigation, which is now nearly completed, may, we hope, form the subject of a second communication.

#### APPENDIX,

*containing a Theoretical Discussion of some cases of Chemical Change.*

*By WILLIAM ESSON, M.A., Fellow of Merton College, Oxford.*

THE most simple case of chemical change occurs in a system in which a single substance is undergoing change in presence of a constant quantity of other substances, and at a constant temperature. A practical constancy of the other substances is obtained by having them present in large excess; for any change produced in their amount by reason of the change of the single substance is infinitesimal in comparison with their original amount, and its effect on the system may therefore be neglected.

By a "system" is meant a unit of volume in which given quantities of substances are present; these quantities are called "elements of the system;" "a system in which a single substance is undergoing change," is a system in which the variation of the other substances does not affect the change of the single substance.

It has been ascertained by experiment that the residue  $y$  of the substance undergoing change in a system of this kind, is connected with the time  $x$  during which the change has been proceeding, by the following equation,

$$y = ae^{-\alpha x}, \dots \dots \dots \dots \dots \dots \dots \dots \dots \quad (1)$$

$a$  being the quantity of the substance in the system at the commencement of the change, and  $\alpha$  a constant, the meaning of which may be thus determined; differentiating (1) and eliminating  $x$ , we have

$$\frac{dy}{dx} = -\alpha y. \dots \dots \dots \dots \dots \dots \dots \dots \dots \quad (2)$$

Now  $-\frac{dy}{dx}$  is the amount of substance which disappears in a unit of time at the time  $x$ , when  $y$  is the quantity of substance present in the system, and the equation (2) expresses the law that "the amount of change in a unit of time is directly proportional to the quantity of substance;" following the analogy of the motion of a material particle, we

may call  $\frac{dy}{dx}$  the rate or velocity of chemical change, and the law may be thus stated:— “The velocity of chemical change is directly proportional to the quantity of substance undergoing change.”

The constant  $\alpha$  expresses the fraction of the substance which is changed in a unit of time; this fraction depends upon the other elements of the system, and upon its physical conditions, such as temperature, density, &c. By varying each of these conditions in succession, it is possible to determine  $\alpha$  as a function of them, and to predict the progress of the chemical change of a single substance, from its commencement to its completion, under any assignable conditions.

This simple case of chemical change is of comparatively rare occurrence. Two instances of it are recorded in the preceding pages (pp. 209 & 210,  $n=3$ ). It is necessary therefore to investigate the modifications which the general law undergoes in the case of complex reactions.

Let us first take the case in which the chemical change consists of the reaction of two substances, neither of which is present in the system in great excess. In the discussion of this case we shall assume the general truth of the law of variation of the rate of chemical action, which has been derived from experiments in which the constancy of all the elements but one has been secured by taking them in excess. In fact we shall assume that the truth of the law depends only upon the constancy of the elements, and not upon their excess. Since, then, the velocity of change of each substance is proportional to its quantity when the quantity of the other is constant, it follows that the velocity of change is proportional to the product of the quantities when both vary. Let  $a, b$  be the number of equivalents of the substances present in the system at the commencement of the reaction,  $z$  the number of equivalents of each which has disappeared during a time  $x$ , then  $a-z, b-z$  are the number of equivalents remaining at the end of that time; hence

$$\frac{dz}{dx} = n(a-z)(b-z), \quad \dots \dots \dots \dots \dots \dots \dots \quad (3)$$

the solution of which is

$$\log \left(1 - \frac{z}{a}\right) - \log \left(1 - \frac{z}{b}\right) = n(a-b)x, \quad \dots \dots \dots \dots \quad (4)$$

an equation for determining the amount of chemical change, in this case, after the lapse of a given time.

When the substances are originally present in equivalent quantities,  $a=b$ , and (3) becomes

$$\frac{dz}{dx} = n(a-z)^2, \quad \dots \dots \dots \dots \dots \dots \dots \quad (5)$$

the solution of which is

$$z = a \frac{nax}{nax+1}. \quad \dots \dots \dots \dots \dots \dots \dots \quad (6)$$

The equation connecting the residue  $y$  with the time is in this case

$$y = \frac{a}{nax+1}; \quad \dots \dots \dots \dots \dots \dots \dots \quad (7)$$

and if at the commencement of the reaction the substances had been present in infinitely large quantities,

$$y = \frac{1}{nx} \cdot \dots \dots \dots \dots \dots \dots \dots \quad (8)$$

The curve (6), which expresses the reaction of two substances originally present in equivalent quantities, is a rectangular hyperbola, and when the original quantities are infinite, the residue varies inversely as the time. This result has been already referred to at pages 202 & 203, where experimental evidence of the relation has been adduced. That evidence is, however, somewhat impaired by the fact that the numbers which express the percentage of chemical change during the first four or five minutes fail to satisfy this relation; but it may be shown that this failure is probably due to the gradual formation of one of the substances which take part in the reaction.

Let us suppose that at the commencement of the reaction there are present  $\alpha$  equivalents of a substance A, which during the course of the reaction is gradually changed into an equivalent quantity of a substance B, and that B reacts with a substance C of which  $\alpha$  equivalents are originally present; also let  $u$  be the number of equivalents of A which remain after an interval  $x$ , and  $v$  the number of equivalents of B which remain after the same interval; then, since the velocity of diminution of  $u$  is proportional to its quantity, and the velocity of diminution of  $v$  proportional to the product of its quantity into the quantity of  $c$ , and the velocity of increase of  $v$  equal to the velocity of diminution of  $u$ , we have the following equations,

$$\frac{du}{dx} = -\beta u, \quad \dots \dots \dots \dots \dots \dots \dots \quad (9)$$

$$\frac{dv}{dx} = -\alpha v(u+v) + \beta u. \quad \dots \dots \dots \dots \dots \dots \dots \quad (10)$$

The solution of (9) is

$$u = ae^{-\beta x}; \quad \dots \dots \dots \dots \dots \dots \dots \quad (11)$$

so that if the residue of  $u$  could be measured separately from that of  $v$ , the rate of change of  $u$  into  $v$  could be determined, but in the actual experiments  $u$  and  $v$  are determined together, and the relation between the total residue  $y (=u+v)$  and the duration of the reaction  $x$  is consequently very complex.

Adding (9) and (10), we have,

$$\frac{dy}{dx} + \alpha vy = 0; \quad \dots \dots \dots \dots \dots \dots \dots \quad (12)$$

substituting for  $dx$  from (9), and for  $v$  its value  $y-u$ , we obtain the equation

$$\frac{dy}{y^2 du} + \frac{\alpha}{\beta y} - \frac{\alpha}{\beta u} = 0, \quad \dots \dots \dots \dots \dots \dots \dots \quad (13)$$

the solution of which is

$$\frac{\alpha}{\beta} e^{\frac{\alpha}{\beta} u} \left\{ c - \log u + \frac{\alpha}{\beta} u - \frac{1}{1.2^2} \left( \frac{\alpha}{\beta} u \right)^2 + \dots \right\} y = 1. \quad \dots \dots \dots \dots \quad (14)$$

If we replace for  $u$  its value  $ae^{-\beta x}$ , we obtain an equation connecting the residue  $y$  with

the time  $x$ . In the experiments to which this hypothesis is applicable (p. 204), the value of  $u$  becomes inappreciable after the action has gone on for about six minutes, so that after that time the course of the action satisfies the relation,

$$\frac{\alpha}{\beta}(c - \log a + \beta x)y = 1, \dots \dots \dots \dots \quad (15)$$

or

$$(c' + x)y = \frac{1}{\alpha}. \dots \dots \dots \dots \dots \dots \quad (16)$$

An equation of the form (16) is satisfied by all the numbers recorded in page 203 after  $x=6$ , the values of  $c'$  and  $\frac{1}{\alpha}$  being 0·1 and 157. Assuming for  $\beta$  the value 69, we obtain for  $c$  the value 4·68. Substituting these values in (14), we obtain the following series of numbers for the values of  $y$  between 2 and 6. The earlier numbers are omitted because the experimental values of  $y$  exhibit an irregularity, which is probably due to errors of experiment which occur in short intervals of time less than one minute. The numbers after  $x=6$ , obtained from the equation  $(x+1)y=157$ , are given at p. 203.

$x.$	$y.$	
	Found.	Calculated.
2	51·9	51·6
3	42·4	42·9
4	35·4	35·4
5	29·8	29·7

Considering the experimental evidence, and the fair agreement of the numbers in the preceding Table, there seems to be sufficient ground for believing that in this case the chemical change consists of the gradual formation of a substance which at the same time slowly disappears by reason of its reaction with a proportional quantity of another substance.

The rate of formation of the substance, and the fraction  $\beta$  which is formed in a unit of time, depend upon the conditions of the system, just in the same way as its rate of decomposition depends upon these conditions. It would, however, be a hopeless task to attempt to discover the relation between  $\alpha$ ,  $\beta$  and the conditions of the system, when we have to deal with a series of complex equations like (14). This complexity explains the failure to discover any simple relation in the case of the variation of sulphuric acid referred to at p. 195.

The next case to be considered is that of a system in which there are two substances undergoing change in presence of a large excess of the other elements of the system. If both substances are present in the system from the commencement of the change and are independent of each other, the velocity of diminution of each is proportional to its quantity, and their residues accord with the simple law  $y = ae^{-\alpha x}$ ; and if both these residues are measured together, the equation of the reaction is

$$y = a_1 e^{-\alpha_1 x} + a_2 e^{-\alpha_2 x}, \dots \dots \dots \dots \dots \dots \quad (17)$$

2 H 2

$a_1, a_2$  being the quantities of the substances originally introduced into the system, and  $\alpha_1, \alpha_2$  the fractions of them which disappear in a unit of time.

If, however, the substances are not independent, but are such that one of them is gradually formed from the other, we have a different system of equations to represent the reaction.

Let  $u, v$  be the residues of the substances after an interval  $x$ ,  $y (= u+v)$  being the total residue actually measured at that time. Let the initial values of  $u$  and  $v$  be  $u=a$ ,  $v=0$ ; let  $\alpha u$  be the rate of diminution of  $u$  due to its reaction with one of the other elements of the system, and  $\beta u$  its rate of diminution due to its reaction with another of the elements of the system, by means of which  $v$  is formed, and let  $\gamma v$  be the rate of diminution of  $v$ , then

$$\frac{du}{dx} = -(\alpha + \beta)u, \quad \dots \dots \dots \dots \dots \dots \quad (18)$$

$$\frac{dv}{dx} = \beta u - \gamma v, \quad \dots \dots \dots \dots \dots \dots \quad (19)$$

whence

$$u = ae^{-(\alpha+\beta)x}, \quad \dots \dots \dots \dots \dots \dots \dots \dots \quad (20)$$

$$v = \frac{\alpha\beta}{\alpha + \beta - \gamma} \{ e^{-\gamma x} - e^{-(\alpha+\beta)x} \}, \quad \dots \dots \dots \dots \dots \dots \quad (21)$$

$$y = \frac{a}{\alpha + \beta - \gamma} \{ \beta e^{-\gamma x} + (\alpha - \gamma) e^{-(\alpha+\beta)x} \}. \quad \dots \dots \dots \dots \quad (22)$$

There are several particular cases of these equations which require to be considered separately.

(1)  $\beta=0$ . Fraction of  $v$  formed=0.

In this case the system of equations reduce to

$$u = ae^{-\alpha x},$$

$$v = 0,$$

$$y = ae^{-\alpha x}.$$

The experimental case corresponding to this is that recorded on page 209.

(2)  $\gamma > \alpha$ . Fraction of  $v$  decomposed in a unit of time, greater than the fraction of  $u$  decomposed in a unit of time.

In this case the last equation of the system is of the form

$$y = a_1 e^{-\alpha_1 x} - a_2 e^{-\alpha_2 x}.$$

The experimental case corresponding to this is that recorded on pages 210, 215,  $n=1$ .

(3)  $\gamma = \alpha$ . The fraction of  $v$  decomposed in a unit of time equal to the fraction of  $u$  decomposed in a unit of time.

In this case the last equation of the system reduces to the form

$$y = ae^{-\alpha x}.$$

The experimental case corresponding to this is recorded on pages 210, 215,  $n=3$ .

(4)  $\gamma < \alpha$ . The fraction of  $v$  decomposed in a unit of time greater than the fraction of  $u$  decomposed in a unit of time.

In this case the last equation of the system is of the form

$$y = a_1 e^{-\alpha_1 x} + a_2 e^{-\alpha_2 x}.$$

The experimental cases corresponding to this are recorded on pages 210, 215,  $n=4, 6, 8, 10$ .

It is thus possible to have all these four cases in succession in a set of experiments in which only one condition is progressively varied, provided that the variation of  $\gamma$  and  $\alpha$  is such that  $\gamma$  is at first greater than  $\alpha$ , but increases in a less ratio than  $\alpha$ . Several attempts have been made to calculate equations of the form  $y = a_1 e^{-\alpha_1 x} \pm a_2 e^{-\alpha_2 x}$  which should give the experimental numbers within the errors of experiment, and at the same time yield values of the fractions  $\alpha, \beta, \gamma$  from which the law of their variation with a variable quantity of sulphuric acid could be discovered. Some of these equations are recorded on page 214. The number and exactness of the experimental results are, however, not sufficient to enable us to extract from the complicated equation

$$y = \frac{a}{\alpha + \beta - \gamma} \{ \beta e^{-\gamma x} + (\alpha - \gamma) e^{-(\alpha + \beta)x} \}$$

trustworthy values of  $\alpha, \beta, \gamma$ , and this inexactness precludes the possibility of investigating the law of their variation when the conditions of the experiment are varied. What we can state with certainty is, that the numbers are all satisfied by equations of the forms

$$y = a_1 e^{-\alpha_1 x} - a_2 e^{-\alpha_2 x},$$

$$y = a e^{-\alpha x},$$

$$y = a_1 e^{-\alpha_1 x} + a_2 e^{-\alpha_2 x},$$

and that successive sets of numbers, obtained by varying one condition progressively, are satisfied by these successive forms of equations. These forms, and the order of their succession, are accounted for by a hypothesis for which there is considerable experimental evidence, and it is thus highly probable that the results arrived at in the above discussion give a true account of the progress of the reaction.

The law of variation of  $\alpha, \beta, \gamma$  with the conditions of the system will probably be detected when the case in which  $\beta, \gamma$  both vanish for all conditions of the system, has been fully discussed.

A complete investigation of this case is reserved for a future communication.

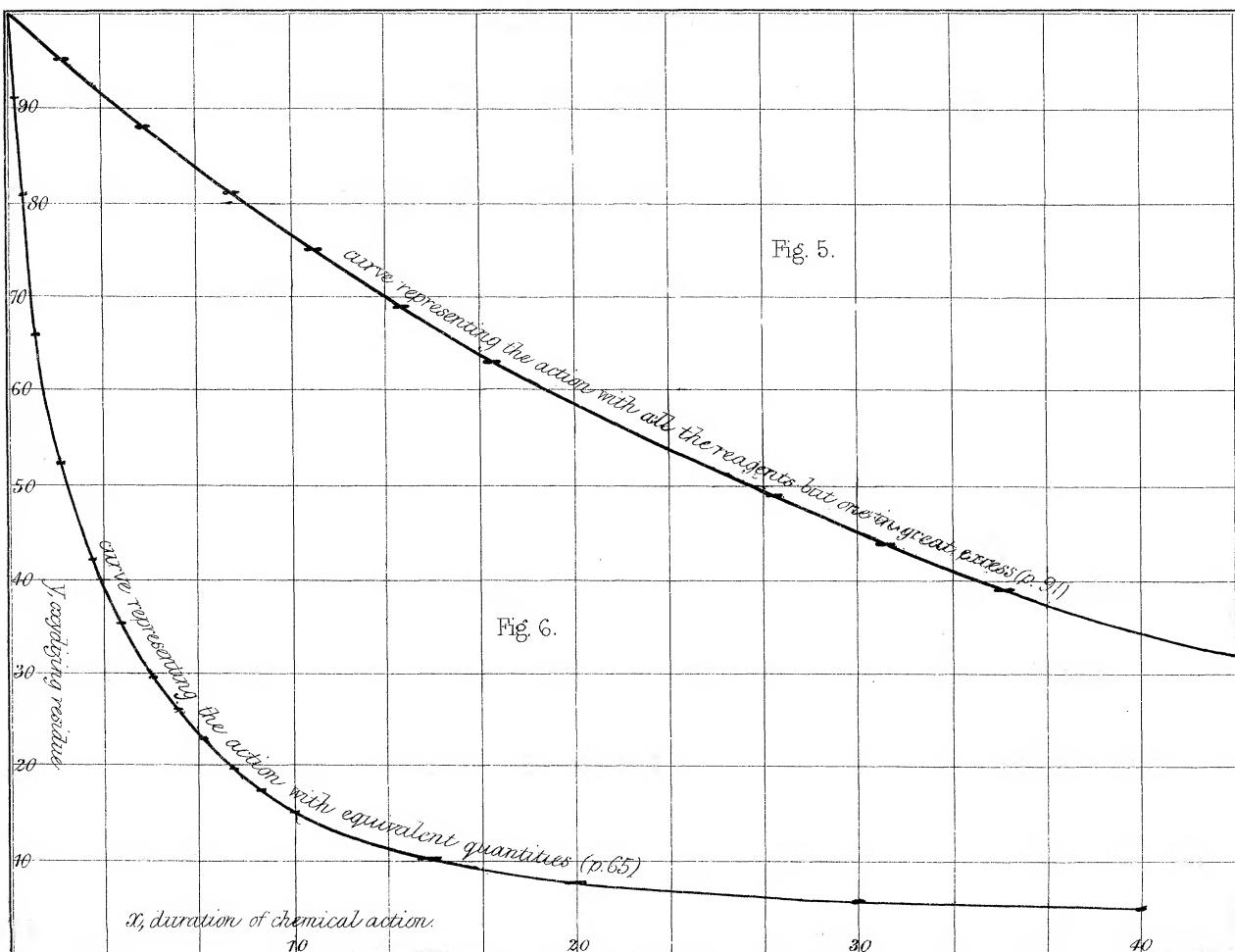
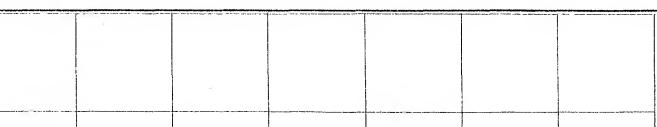
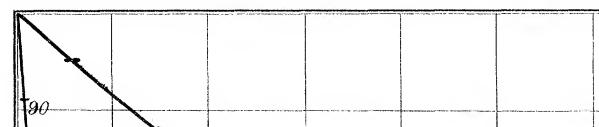
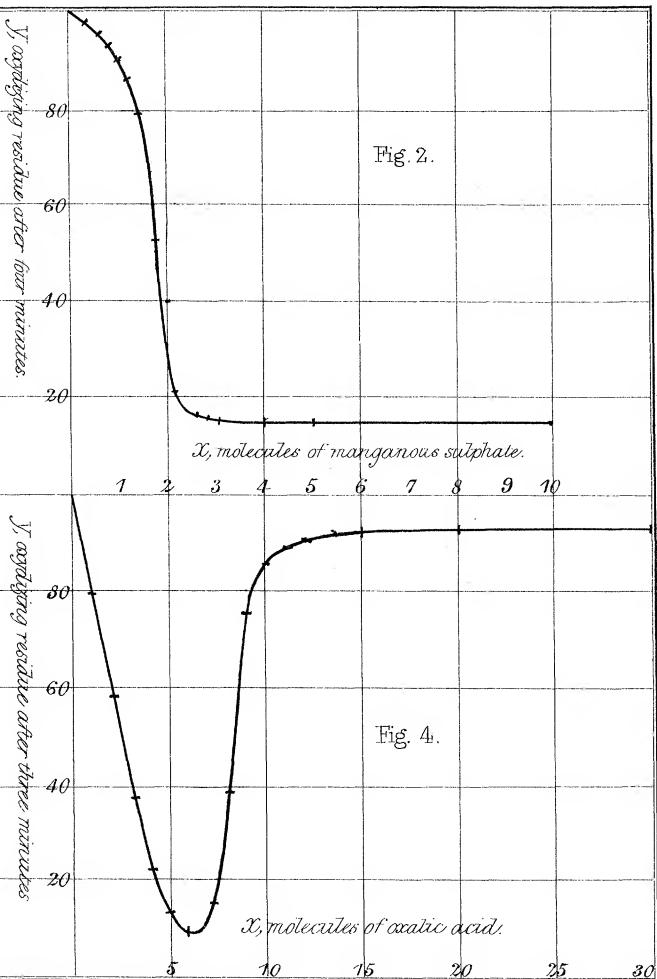
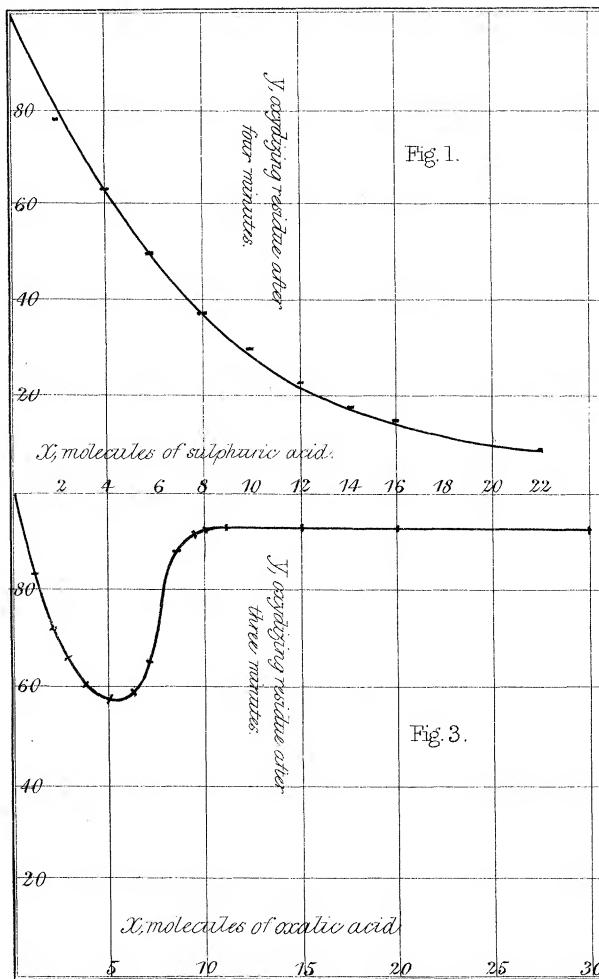


Fig. 6.

